

The Affinity Constants of Amphoteric Electrolytes. I. Methyl Derivatives of Para-aminobenzoic Acid and of Glycine

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Proc. R. Soc. Lond. A 1906 **78**, 82-102

doi: 10.1098/rspa.1906.0062

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The Affinity Constants of Amphoteric Electrolytes. I.—Methyl Derivatives of Para-aminobenzoic Acid and of Glycine.

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(Communicated by Professor James Walker, F.R.S. Received May 21,—Read May 31, 1906.)

(From the Chemical Laboratory, University College, Dundee.)

The following investigation was undertaken in order to determine the influence on the basic and acidic constants of successive introductions of a methyl group into an amino-acid, including the effect of changing the acid into the corresponding methyl ester. Two series of compounds were investigated, namely, the methyl derivatives of *p*-aminobenzoic acid and of glycine. Constants for *p*-aminobenzoic acid, glycine, and some of its methyl derivatives had already been determined by Winkelblech.*

Methods.

Whenever practicable the basic constant k_b was determined by means of the catalysis of methyl acetate, using the comparison method of Walker and Wood.† The end point was determined in a separate experiment with decinormal hydrochloric acid; and it was found that the same result was obtained whether or not the bottle containing the reaction mixture had been opened to admit of intermediate readings being taken. In every case 1 c.c. at a time was withdrawn and titrated with N/20 caustic soda, which had been prepared from sodium and conductivity water; and unless otherwise stated, phenolphthalein was used as indicator.

In the tables v refers to the dilution of the solution after mixture, A is the total range of the reaction, and c is the constant for a monomolecular reaction.

In cases where the catalysis method was inapplicable, recourse was had to the Löwenherz solubility method, which was carried out as follows: A flask containing a known weight of substance mixed with a known volume of standard hydrochloric acid was kept in the thermostat for at least a day, being shaken from time to time. The liquid was then filtered through a tared paper, and the paper and contents—the amount left undissolved—were dried until of constant weight. The solubility in water was determined by a similar method.‡

* 'Zeit. für physikal. Chem.,' vol. 36, p. 546, 1901.

† 'Journ. Chem. Soc.,' vol. 83, p. 484, 1903.

‡ Compare Wood, 'Journ. Chem. Soc.,' vol. 83, p. 572, 1903.

The Affinity Constants of Amphoteric Electrolytes. 83

In one case, owing to the impracticability of either of the above methods, the basic constant was determined by the distribution method of Farmer and Warth.* Known weights of substance were shaken up with known volumes of benzene and water, and of benzene and standard hydrochloric acid. The amount of free base present in the benzene layer was determined by experiment, allowance being made for the mutual solubility of benzene and water; the amount of base in the aqueous layer was obtained by difference. From the data obtained in this way, the basic constant, k_b , was calculated.

The acidic constant k_a was determined by means of conductivity measurements or by the salt-hydrolysis method of Shields.†

The conductivity measurements were effected in the usual way, but it was found that in most cases unplatinised electrodes gave better results than platinised electrodes, owing, apparently, to a certain amount of absorption of the substance by the latter. The water used had a conductivity not greater than 1.5×10^{-6} at 25° ; no correction was made for the conductivity of the water. From the measurements the acidic constant was calculated by means of the equations established by Walker.‡ The symbols used have the same significations as in those papers.

The solution for the hydrolysis method of Shields was prepared as follows. To a measured volume of a standard solution of pure soda was added the equivalent quantity of the substance. When this solution had reached the temperature of the thermostat, the equivalent amount of a solution of methyl acetate—also at 25° —was added. After shaking, 5 c.c. of the mixture was immediately withdrawn and titrated with 0.0252 N hydrochloric acid, using nitrophenol as indicator. When the reaction proceeded very rapidly, this initial titre was obtained by calculation. At suitable intervals, other portions of 5 c.c. were withdrawn and titrated similarly.§

As equivalent concentrations of salt and methyl acetate were employed, the calculation is somewhat simpler than that given by Shields. If E is the original concentration of methyl acetate and of the salt, x the amount transformed in time t , c the constant regulating the equilibrium between the hydrolysed and unhydrolysed portions of the salt, and k the saponification constant for caustic soda, then

$$kc \, dt = \frac{x \, dx}{(E-x)^2},$$

* 'Journ. Chem. Soc.,' vol. 85, p. 1713, 1904.

† 'Zeit. physikal. Chem.,' vol. 12, p. 167, 1893.

‡ 'Roy. Soc. Proc.,' vol. 73, p. 155, vol. 74, p. 271, 1904.

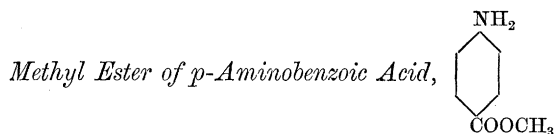
§ Cf. Shields, *loc. cit.*

which on integration between the proper limits gives

$$c = \frac{1}{kt} \left[\frac{E}{E-x} - 1 - 2.303 \log_{10} \frac{E}{E-x} \right].$$

The value of k_a is obtained from the equation $k_a = K/c$, in which K is the dissociation constant of water, and is equal to 1.21×10^{-14} at 25° . The use of the above formula is inadmissible when the degree of hydrolysis is great. This is the case with the betaines investigated. These were compared directly with a similar solution of pure caustic soda; and the rates of reaction in the two cases proved to be almost identical.

The experiments throughout the investigation were carried out at a temperature of 25° .



A solution of the acid in absolute methyl alcohol was saturated with hydrochloric acid gas, and boiled under a reflux condenser for five hours. On cooling, crystals of the ester hydrochloride separated, which, on recrystallisation from methyl alcohol, yielded plates of a slightly yellowish colour.

Chlorine found..... I, 19.0; II, 18.86 per cent.

$C_6H_4(COOCH_3)NH_2HCl$ requires Cl 18.93 ,,

The amount of halogen was in this and in all similar cases determined by Volhard's method.

On neutralising a solution of the hydrochloride with ammonia, the ester was precipitated, and was recrystallised from methyl alcohol as white plates melting at 112° .*

Comparison Solutions.

N/15 Cl solution (20 per cent. HCl, 80 per cent. KCl) $c = 0.0000380$

„ „ (30 „ 70 „ „) $c = 0.0000570$

Hydrolysis in I = $20 \times \frac{457}{380}$; in II = $30 \times \frac{452}{570}$.

= 24.05 per cent. = 23.8 per cent.

Now if x is the hydrolysed proportion, v the dilution, and K the dissociation constant for water,

$$\frac{k_b}{K} = \frac{(1-x)v}{x^2}.$$

* Compare Einhorn, 'Liebig's Annalen,' vol. 311, p. 158, 1900.

Hence

$$\begin{array}{ll} \text{I.} & \text{II.} \\ \frac{k_b}{K} = \frac{0.76 \times 15}{(0.24)^2}; & \frac{k_b}{K} = \frac{0.762 \times 15}{(0.238)^2}. \\ = 198. & = 202. \end{array}$$

Mean value for $k_b/K = 200$.

Determination of Basic Constant—Catalysis Method.

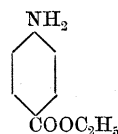
0.1875 gramme hydrochloride in 15 c.c. water, 1 c.c. MeAc, $v = 15$, $A = 15.40$.

I.

t .	Titre.	x .	$A - x$.	c .
0	1.27	0	15.40	—
2265	4.50	3.23	12.17	0.0000452
2474	4.80	3.53	11.87	457
2866	5.31	4.04	11.36	461
3725	6.23	4.96	10.44	453
4021	6.59	5.32	10.08	458
4348	6.90	5.63	9.77	454
5158	7.74	6.47	8.93	458
5452	7.98	6.71	8.69	456
5741	8.30	7.03	8.37	461
6581	9.00	7.73	7.67	460
Mean				0.0000457

II.

t .	Titre.	x .	$A - x$.	c .
0	1.22	0	15.40	—
1506	3.46	2.24	13.16	0.0000454
2621	4.88	3.66	11.74	449
2957	5.30	4.08	11.32	452
4016	6.48	5.26	10.14	452
4450	6.90	5.68	9.72	449
5430	7.89	6.67	8.73	454
Mean				0.0000452

Ethyl Ester of p-Aminobenzoic Acid,

This substance was prepared by a method analogous to that adopted for the methyl ester. The hydrochloride, when recrystallised from methyl

alcohol, separated in shining white plates, which melted at 206° to 207° with decomposition.

Chlorine found..... 17.48 per cent.

$C_6H_4(COOC_2H_5)NH_2HCl$ requires Cl..... 17.62 „

The ester was liberated by treatment of the hydrochloride with ammonia.

It recrystallised from aqueous alcohol in the form of fine white needles melting at 91° .

Determination of Basic Constant—Catalysis Method.

0.2015 gramme hydrochloride in 20 c.c. water, 1 c.c. MeAc, $v = 20$,

$$A = 12.07.$$

I.

t .	Titre.	x .	$A - x$.	c .
0	0.98	0	12.07	—
2.422	3.20	2.22	9.85	0.0000364
5.337	5.30	4.32	7.75	360
5.682	5.57	4.59	7.48	366
6.742	6.20	5.22	6.85	365
7.267	6.46	5.48	6.59	362
8.189	6.97	5.99	6.08	364
8.755	7.29	6.31	5.74	369
9.644	7.70	6.72	5.35	366
10.002	7.85	6.87	5.20	366
Mean				0.0000365

II.

t .	Titre.	x .	$A - x$.	c .
0	0.98	0	12.07	—
2.744	3.43	2.45	9.62	0.0000359
3.088	3.75	2.77	9.30	366
4.148	4.50	3.52	8.55	360
4.674	4.86	3.88	8.19	360
5.596	5.46	4.48	7.59	360
6.162	5.83	4.85	7.22	362
7.051	6.35	5.37	6.70	362
7.409	6.55	5.57	6.50	363
Mean				0.0000361

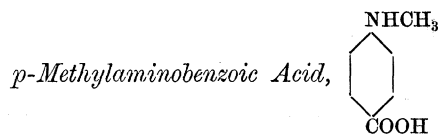
Comparison Solutions.

N/20 Cl solution (25 per cent. HCl, 75 per cent. KCl), $c = 0.0000361$.

„ „ (20 „ 80 „), $c = 0.0000290$.

Hence $k_b/K = I, 236$; $II, 240$.

Mean value of $k_b/K = 238$.



Twenty-five grammes of *p*-aminobenzoic acid were dissolved in the equivalent quantity of an aqueous solution of caustic soda of about 8 per cent. strength. To the cooled solution, one equivalent of methyl sulphate was added, and the mixture was kept cool, and shaken from time to time. After one and a half hours the reaction was practically complete, the mixture having become quite pasty. The solid was filtered off on the pump, dried and recrystallised from boiling water. The yield of crude substance was almost quantitative. When recrystallised, it consisted of small white needles, which on drying turned slightly yellow, melting at 144° to 145° ; and this melting point remained unchanged after recrystallising twice from water, alcohol, or benzene.

0.2028 gramme substance gave 0.4716 gramme CO_2 and 0.1076 gramme H_2O .

I. 0.2645 gave 20.3 c.c. moist N, measured at 16° and 764 mm.

II. 0.2420 „ 18.6 „ „ „ 15 „ 773 „

	C.	H.	N.
	per cent.	per cent.	per cent.
Found	63.42	5.90	I, 9.0 II, 9.15
$\text{C}_6\text{H}_4(\text{NHCH}_3)(\text{COOH})$ requires	63.57	5.96	9.29

As the direct determination of nitrogen in the case of the aminobenzoic acids tends to give low results, the percentage of nitrogen was redetermined by Kjeldahl's method.

0.4605 gramme gave ammonia equivalent to 0.0431 gramme N = 9.37 per cent.

The same product was also obtained by the action of methyl iodide on *p*-aminobenzoic acid, but the yield was much smaller, and the isolation and purification of the acid were more troublesome.

p-Methylaminobenzoic acid has an acid reaction to ordinary indicators, and can be roughly titrated by means of *o*-nitrophenol, which changes colour when about 94 per cent. of the acid present has been neutralised.

It is soluble in alcohol and benzene, though not very soluble in cold water, and is to a slight extent volatile in steam. The alkali salts are freely soluble in water; and from their aqueous solutions the free acid can be recovered by the cautious addition of hydrochloric acid, excess of which must be avoided, since it redissolves the acid with formation of the hydrochloride.

Determination of the Basic Constant—A. Catalysis Method.

I.

0.151 gramme acid in 11.5 c.c. N/10 HCl and 22 c.c. water, 2 c.c. MeAc,

$$v = 33.5, A = 12.70.$$

<i>t.</i>	Titre.	<i>x.</i>	<i>A - x.</i>	<i>c.</i>
0	1.15	0	12.70	—
3,225	4.60	3.45	9.25	0.0000427
4,674	5.85	4.70	8.00	429
5,709	6.60	5.45	7.25	426
7,141	7.52	6.37	6.33	424
8,594	8.38	7.23	5.47	426
8,770	8.43	7.28	5.42	422
8,992	8.57	7.42	5.28	424
10,025	9.08	7.93	4.77	424
12,925	10.24	9.09	3.61	423
Mean.....				0.0000425

N/33.5 Cl solution (52 per cent. HCl, 48 per cent. KCl) $c = 0.0000454$.Therefore relative concentration of free HCl = $\frac{0.52 \times 425}{454}$ 0.487

" " salt..... 0.663

" " free base $C_6H_4(NHCH_3)COOH$... 0.337

whence $\frac{k_b}{K} = \frac{33.5 \times 0.663}{0.487 \times 0.337} = 135.$

II.

0.151 gramme acid in 12.2 c.c. N/10 HCl and 20 c.c. water, 2 c.c. MeAc,

$$v = 32.2, A = 13.24.$$

<i>t.</i>	Titre.	<i>x.</i>	<i>A - x.</i>	<i>c.</i>
0	1.31	0	13.24	—
2847	4.72	3.41	9.83	0.0000454
3947	5.72	4.41	8.83	446
4295	6.13	4.82	8.42	458
5341	7.04	5.73	7.51	460
5656	7.33	6.02	7.22	466
5775	7.38	6.07	7.17	460
6770	8.15	6.84	6.40	466
9661	9.75	8.44	4.80	456
Mean.....				0.0000458

N/32.2 Cl solution (53 per cent. HCl, 47 per cent. KCl), $c = 0.0000476$.

$$\frac{k_b}{K} = \frac{32.2 \times 0.71}{0.51 \times 0.29} = 154.$$

B. Löwenherz Solubility Method.

Amount dissolved by 1000 c.c. water	1.79 grammes.
Whence concentration of base in water (solubility)	0.0119 N.
Amount dissolved by 50 c.c. 0.1022-N HCl.....	0.549 gramme.
Whence total concentration of base $C_6H_4(NHCH_3)COOH$	0.0727 N.
Therefore concentration of salt	0.0608 N.
And concentration of free HCl	0.0414 N.

$$\frac{k_b}{K} = \frac{0.0608}{0.0119 \times 0.0414} = 124.$$

General mean of $k_b/K = 137$.

Determination of the Acidic Constant k_a —Conductivity Method.

Conductivity of the Sodium Salt.—As the salt does not crystallise well, the solutions were made up by adding the calculated quantity of acid to a standard solution of soda, made from sodium and CO_2 -free water.

v	32	64	128	256	512	1024
μ , I	68.2	71.6	72.9	75.3	77.3	80.5
II	68.5	71.7	72.7	75.5	77.6	81.0

The figures under I and II were obtained from distinct solutions: from the above $\mu_{1024} - \mu_{32} = 12.4$, which is about the normal value for non-hydrolysed sodium salts.

The speeds of the hydrogen and sodium ions are 347 and 51 respectively: so that

$$\mu_{\infty} H^+, XOH^- = 81 + 347 - 51 = 377,$$

and

$$\mu_{\infty} HX^+, XOH^- = (81 - 51) + (81 - 51 + 6) = 66.$$

For the method of obtaining the value of $\mu_{\infty} HX^+, XOH^-$, compare Walker.*

Conductivity of the Acid.—Sample I was recrystallised from water, sample II from benzene. The solution at each dilution was made up separately, as the use of pipettes is not advisable when dealing with solutions of such feeble conducting power.

v .	μ .		m .	$k_0 \times 10^5$.
	I.	II.		
128	10.2	10.2	0.0271	0.59
256	15.6	15.6	0.0415	0.70
512	23.7	23.6	0.0629	0.82
1024	34.1	34.2	0.0908	0.88

* *Loc. cit.*

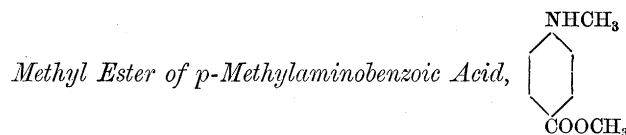
It is evident that the Ostwald "dissociation constant" k_0 has here no real application, since it rises by 50 per cent. in the comparatively small range of dilutions studied.

Conductivities calculated from Walker's equations.

$$k_a = 0.92 \times 10^{-5}, k_b/K = 137, \mu_{\infty} \text{H}^+, \text{XOH}^- = 377, \mu_{\infty} \text{HX}^+, \text{XOH}^- = 66,$$

$v.$	$a.$	$d.$	$\mu.$	$m.$	$k_0 \times 10^5.$
128	18.3×10^{-5}	18.2×10^{-5}	10.3	0.0275	0.61
256	14.9	7.4	15.6	0.0415	0.70
512	11.5	2.8	23.1	0.0614	0.79
1024	8.5	1.0	33.5	0.0891	0.85

The divergence between the experimental and the calculated values of μ does not exceed the conductivity of the solvent water.



was prepared by an analogous method to that given on p. 84. In this case, however, the hydrochloride did not separate out, and the ester was precipitated by means of sodium carbonate. It crystallised from ligroin in the form of small white plates, melting at 75° to 76° .

0.1860 gramme gave ammonia equivalent to 0.0155 gramme N ...	8.35
$\text{C}_6\text{H}_4(\text{NHCH}_3)(\text{COOCH}_3)$ requires N	8.48

This substance is soluble in benzene, alcohol, and ether, although it does not crystallise well from them, but it is almost insoluble in water.

Determination of Basic Constant—Distribution Method.

Amount of benzene layer.	Amount of aqueous layer.	Total base taken.	Base in benzene layer.	Base in aqueous layer.	Distribution ratio = F.
Distribution between benzene and water.					
c.c. 14.7	c.c. 500	gramme. 0.1308	gramme. 0.1073	gramme. 0.0235	157
14.7	490	0.1815	0.1505	0.0310	163
Distribution between benzene and 0.1022 N HCl.					
I c.c. 10	c.c. 95	gramme. 0.3005	gramme. 0.146	gramme. 0.1545	—
II 10	95	0.2500	0.126	0.124	—

1906.] *The Affinity Constants of Amphoteric Electrolytes.* 91

From I—

$$\text{Concentration of free base in water} = \frac{0.0146}{160 \times 0.165} \dots\dots\dots 0.00055 \text{ N.}$$

$$\text{Concentration of total base} \dots\dots\dots 0.00986 \text{ N.}$$

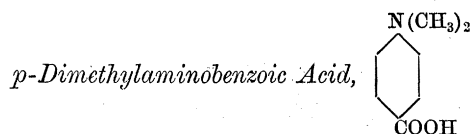
$$\text{Whence concentration of salt is } 0.00932 \text{ N, and of acid } \dots\dots\dots 0.0929 \text{ N.}$$

$$\text{Therefore } \frac{k_b}{K} = \frac{0.00932}{0.0929 \times 0.00055} \dots\dots\dots 182.$$

Similarly, from II—

$$\frac{k_b}{K} = \frac{0.00744}{0.0948 \times 0.000476} \dots\dots\dots 164.$$

$$\text{Mean value of } k_b/K = 173.$$



By the action of methyl sulphate upon the crude *p*-methylaminobenzoic acid the process of methylation can be carried one step further. The mode of procedure is identical with that described for the preparation of the monomethyl acid. By recrystallising the product from 50 per cent. aqueous alcohol, *p*-dimethylaminobenzoic acid separates out in fine white needles, which melt at 235° to 236° , and are identical with the product obtained by the action of phosgene on dimethylaniline.* The yield is practically quantitative.

p-Dimethylaminobenzoic acid, though soluble in alcohol, is not very soluble in ether or benzene, and is almost insoluble in water.

Determination of Basic Constant—Solubility Method.

Solubility in Water.

- A. Solution superheated— I, 0.074, II, 0.072 gramme per litre }
 B. „ not superheated—I, 0.074, II, 0.072 „ „ }
 $ = 0.00044 \text{ N.}$

- I. Solubility in 0.100 N HCl = 0.00182 gramme per c.c. = 0.01103 N.
 II. „ 0.1022 N HCl = 0.00186 „ „ = 0.01127 N.

$$\text{From I—} \quad \frac{k_b}{K} = \frac{0.01059}{0.08941 \times 0.00044} = 269.$$

$$\text{And from II—} \quad \frac{k_b}{K} = \frac{0.01083}{0.09137 \times 0.00044} = 269.$$

$$\text{Mean value of } k_b/K = 269.$$

* Michler, 'Berichte,' vol. 9, p. 401, 1876.

Determination of the Acidic Constant.—The only practicable way of effecting this was by conductivity measurements, and this could only be done at one dilution. The Shields method was tried, but the insolubility of the acid prevented accurate titration, and rendered the method invalid.

Conductivity of the Sodium Salt.

v	32	64	128	256	512	1024
μ	67.0	69.7	72.4	74.7	77.1	79.0

The difference, $\mu_{1024} - \mu_{32} = 12$, is again nearly normal, showing that there is not much hydrolysis.

Calculating as on p. 89,

$$\mu_{\infty} \text{H}^+, \text{XOH}^- = 375,$$

$$\text{and } \mu_{\infty} \text{HX}^+, \text{XOH}^- = 62.$$

Conductivity of the Acid.

v .	μ .			m .	k_0 .
	I.	II.	III.		
2260	49.0	49.0	49.0	0.1302	0.86×10^{-5}

I, II, and III were distinct solutions.

Conductivity calculated from $k_a = 0.94 \times 10^{-5}$, $k_b/K = 269$, and from the above values for μ_{∞} .

v .	α .	d .	μ .	m .	k_0 .
2260	56.6×10^{-6}	5.6×10^{-6}	48.9	0.1300	0.86×10^{-5}



This ester was prepared in the same way as the ester of the monomethyl acid; it recrystallises from ethyl alcohol in white plates, melting at 102° .*

Determination of the Basic Constant.—The distribution method was tried, but proved unsatisfactory, owing to the excessive magnitude of the distribution-ratio between benzene and water. The constant was determined by the solubility method.

* Cf. Bischoff, 'Berichte,' vol. 22, p. 343, 1889.

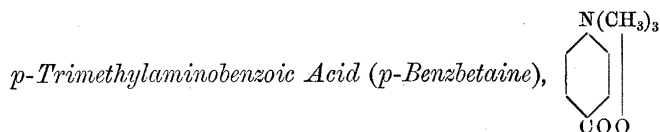
1906.] *The Affinity Constants of Amphoteric Electrolytes.* 93

Solubility in water	= 0.160 gramme per litre		0.00089 N.
I. „	0.0252 N HCl = 1.05 „ „		0.00587 N.
II. „	0.1022 N HCl = 3.76 „ „		0.0210 N.

$$\text{From I—} \quad \frac{k_b}{K} = \frac{0.00498}{0.0202 \times 0.00089} = 277.$$

$$\text{And from II—} \quad \frac{k_b}{K} = \frac{0.0201}{0.0821 \times 0.00089} = 275.$$

Mean value of $k_b/K = 276$.



This substance was prepared by the action of methyl iodide on either *p*-aminobenzoic acid or its dimethyl derivative.* The iodide was recrystallised from water, and decomposed by the action of moist silver hydroxide *in the cold*. If the mixture is heated, a strongly basic substance is obtained, which has not yet been investigated. The benzbetaine was purified by recrystallisation from absolute alcohol, from which it separated in cubes, melting at 255° :—

Iodine found 41.1 per cent.

$C_6H_4 < \begin{smallmatrix} COOH \\ N(CH_3)_3I \end{smallmatrix}$ requires I 41.4 „

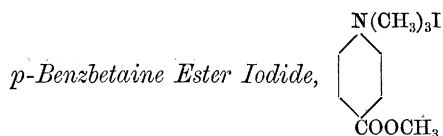
Determination of Basic Constant—Catalysis Method.

0.307 gramme iodide in 15 c.c. water, 1 c.c. MeAc, $v = 15$, $A = 15.40$.

I.

t .	Titre.	x .	$A - x$.	c .
0	1.20	0	15.40	—
2,755	2.52	1.32	14.08	0.0000142
4,160	3.14	1.94	13.46	141
5,665	3.90	2.70	12.70	148
7,035	4.53	3.33	12.07	150
8,505	5.12	3.92	11.48	150
10,055	5.80	4.60	10.80	153
12,788	6.78	5.58	9.82	153
Mean				0.0000148

* Compare Michael and Wing, 'Amer. Chem. Journ.,' vol. 7, p. 195, 1885.



This salt was prepared by heating equivalent quantities of methyl iodide and the methyl ester of *p*-dimethylaminobenzoic acid at 100° for five hours in a sealed tube. On cooling and opening the tube, the mixture was extracted with water. After filtration, the aqueous solution was evaporated down, when the iodide separated. Colourless crystals were obtained by recrystallisation from aqueous alcohol :—

Iodine found 38·8 per cent.

$\text{C}_6\text{H}_4 < \begin{array}{c} \text{N(CH}_3)_3\text{I} \\ \text{COOCH}_3 \end{array}$ requires I 39·6 „

A decinormal solution had an acid reaction to azolitmin, but did not affect methyl orange or congo red.

The catalytic action of an aqueous solution of the iodide on methyl acetate was too slow to yield a definite value for the basic constant of the substance.

Methyl Ester of Glycine, NH₂.CH₂.COOCH₃.

This was prepared in an analogous manner to the other methyl esters. On cooling, crystals of the hydrochloride separated in the form of white plates. After recrystallisation from methyl alcohol, the hydrochloride melts at 175° to 176° with decomposition.

Chlorine found..... 28·42 per cent.

$\text{NH}_2\text{.CH}_2\text{.COOCH}_3\text{.HCl}$ requires Cl 28·29 „

Determination of Basic Constant—Catalysis Method.

I.

0·397 gramme hydrochloride in 15 c.c. water, 1 c.c. MeAc, $v = 4\cdot7$.

<i>t.</i>	Titre.	<i>x.</i>	<i>c.</i>
0	0·30	0	—
7,040	2·55	2·25	0·0000104
9,910	3·65	3·35	110
12,825	4·75	4·45	113
15,880	5·90	5·60	113
17,495	6·65	6·35	116
Mean			0·0000111

II.

0.462 gramme hydrochloride in 15 c.c. water, 1 c.c. MeAc, $v = 4.1$.

t .	Titre.	x .	c .
0	0.20	0	—
5,585	1.95	1.75	0.0000101
8,498	3.10	2.90	110
11,553	4.30	4.10	113
13,168	4.95	4.75	116
Mean			0.0000111

N/15 Cl solution (5 per cent. HCl, 95 per cent. KCl), $c = 0.0000104$.

$$\text{From I—} \quad \frac{k_b}{K} = \frac{0.983 \times 4.7}{0.0167^2} = 16,500.$$

$$\text{And from II—} \quad \frac{k_b}{K} = \frac{0.985 \times 4.1}{0.0146^2} = 18,900.$$

Mean value for $k_b/K = 18,000$ (?).

In these experiments nitrophenol was found to be the best indicator, but was not satisfactory.

Ethyl Ester of Glycine, $\text{NH}_2\text{CH}_2\text{COOC}_2\text{H}_5$.

A specimen of the hydrochloride obtained from Kahlbaum was recrystallised from absolute alcohol.

Chlorine found 25.20 per cent.

$\text{NH}_2\text{CH}_2\text{COOC}_2\text{H}_5\text{HCl}$ requires Cl 25.45 „

A methyl acetate catalysis experiment with the hydrochloride showed that the ethyl ester of glycine was a stronger base than the methyl ester, but the action proceeded too slowly to admit of an accurate calculation of the basic constant.

Dimethylglycine, $\text{N}(\text{CH}_3)_2\text{CH}_2\text{COOH}$.

This substance was prepared according to the method given by Eschweiler.* Equivalent quantities of a 33-per-cent. aqueous solution of dimethylamine and of formaldehyde-cyanhydrin were mixed. After standing for 24 hours the resulting nitrile was extracted with ether, and, after removal of the ether, was saponified with baryta. The barium was removed by means of carbonic anhydride, and the solution was evaporated to dryness. The residue was dissolved in absolute alcohol, from which it afterwards separated in exceedingly hygroscopic crystals, which melted at 157° to 160° .

* 'Liebig's Annalen,' vol. 279, p. 44, 1894.

1906.] *The Affinity Constants of Amphoteric Electrolytes.* 97

0.2080 gramme gave ammonia equivalent to 0.0278

gramme N..... 13.36 per cent.

$N(CH_3)_2CH_2.COOH$ requires N 13.60 „

A sample of the hydrochloride was prepared by treating with hydrochloric acid. On recrystallising it from alcohol, it was obtained in the form of white hygroscopic crystals, melting at 190° with decomposition.

0.192 gramme gave ammonia equivalent to 0.0192

gramme N 10.0 per cent.

Chlorine found 25.28 „

$N(CH_3)_2CH_2.COOH.HCl$ requires N = 10.0, Cl ... 25.45 „

Determination of Basic Constant—Catalysis Method.

I.

0.207 gramme hydrochloride in 15 c.c. water, 1 c.c. MeAc, $v = 10.1$,

$A = 15.40$.

t .	Titre.	x .	$A - x$.	c .
0	1.85	0	15.40	—
1167	4.96	3.11	12.29	0.0000840
1535	5.80	3.95	11.45	839
2996	8.60	6.75	8.65	836
3996	10.10	8.25	7.15	834
6924	13.20	11.35	4.05	838
Mean				0.0000837

N/15 Cl solution (45 per cent. HCl, 55 per cent. KCl), $c = 0.0000881$.

$$\frac{k_b}{K} = \frac{0.712 \times 10.1}{0.288^2} = 87.$$

II.

0.188 gramme hydrochloride in 15 c.c. water, 1 c.c. MeAc, $v = 11.13$,

$A = 15.40$.

t .	Titre.	x .	$A - x$.	c .
0	1.80	0	15.40	—
1238	4.78	2.98	12.42	0.0000754
3742	9.26	7.46	7.94	769
3947	9.60	7.80	7.60	777
4178	9.96	8.16	7.24	784
5200	11.20	9.40	6.00	787
Mean				0.0000774

N/15 Cl solution (40 per cent. HCl, 60 per cent. KCl), $c = 0.0000774$.

$$\frac{k_b}{K} = \frac{0.703 \times 11.13}{0.297^2} = 89.$$

In II the temperature of the thermostat increased slightly during the course of the reaction; the comparison solution was going simultaneously, and was similarly affected.

Mean value of $k_b/K = 88$.

Determination of the Acidic Constant.—The conductivity method was tried, but, owing to the very slight conducting power and to the difficulties attending recrystallisation, it gave too high results; the smallest value of k_a obtained by this means was 2×10^{-7} .

Shields' Method.

0.161 gramme dimethylglycine, 25 c.c. N/16 soda, 10 c.c. MeAc solution,

$$E = \frac{1}{v} = 0.0446.$$

t .	Titre.	x .	$E - x$.	kc .
0	8.70	0	0.0446	—
110	5.75	0.0147	0.0299	0.00084
148	5.35	0.0167	0.0279	89
172	5.15	0.0177	0.0269	89
307	4.45	0.0212	0.0234	86
Mean				0.00087

Whence

$$\frac{k_a}{K} = \frac{k}{kc} = \frac{10.5}{0.00087} = 1.21 \times 10^4, \quad \text{and} \quad k_a = 1.4 \times 10^{-10}.$$

Trimethylglycine (Betaine), $\overline{\text{N}(\text{CH}_3)_3\text{CH}_2\text{COO}}$.

Betaine hydrochloride was obtained by the saponification of betaine ethyl ester hydrochloride, which was effected by boiling for four hours with dilute hydrochloric acid. After partial evaporation of the water, beautiful white crystals of betaine hydrochloride separated out, and were dried in a desiccator :—

Chlorine found 23.15 per cent.
 $\text{N}(\text{CH}_3)_3\text{CH}_2\text{COO.HCl}$ requires Cl..... 23.12 „

Determination of the Basic Constant—Catalysis Method.

I.

0.228 gramme hydrochloride in 15 c.c. water, 1 c.c. MeAc, $v = 10.1$, $A = 15.40$.

t .	Titre.	x .	$A - x$.	c .
0	1.75	0	15.40	—
1425	5.72	3.97	11.43	0.0000909
2595	8.17	6.42	8.98	902
2745	8.44	6.69	8.71	902
2880	8.71	6.96	8.44	907
3060	9.03	7.28	8.12	908
3876	10.31	8.56	6.84	909
Mean				0.0000906

II.

0.271 gramme hydrochloride in 15 c.c. water, 1 c.c. MeAc, $v = 8.5$, $A = 15.40$.

t .	Titre.	x .	$A - x$.	c .
0	2.20	0	15.40	—
1443	6.50	4.30	11.10	0.0000986
1560	6.78	4.58	10.82	983
2562	8.99	6.79	8.61	986
2646	9.17	6.97	8.43	989
Mean				0.0000986

N/15 Cl solution (45 per cent. HCl, 55 per cent. KCl), $c = 0.0000875$.Whence from I—
$$\frac{k_b}{K} = \frac{0.686 \times 10.1}{0.314^2} = 70,$$
and from II—
$$\frac{k_b}{K} = \frac{0.713 \times 8.5}{0.287^2} = 73.$$
Mean value for $k_b/K = 72$.Bredig* from the electrical conductivity calculated the value $k_b/K = 63$.

Determination of the Acidic Constant.—In carrying this out, the hydrochloride was used along with two equivalents of soda, on account of the difficulty in obtaining pure betaine. This, however, answered the purpose equally well, for Shields states that the presence of a neutral salt exerts practically no influence on the velocity of the reaction:—

* 'Zeit. physikal. Chem.,' vol. 13, p. 323, 1894.

A.—25 c.c. N/16 NaOH, 25 c.c. N/16 MeAc, 50 c.c. water. B.—0.241 gramme betaine hydrochloride, 50 c.c. N/16 NaOH, 25 c.c. N/16 MeAc, 25 c.c. water.

<i>t.</i>	Titre.	<i>x.</i>	<i>t.</i>	Titre.	<i>x.</i>
0	12.40	0	0	12.40	0
5	6.50	5.90	5	6.50	5.90
11	4.20	8.20	11	4.35	8.05
13	3.70	8.70	13	3.75	8.65
15	3.27	9.13	15	3.35	9.05

As in the case of *p*-benzbetaine, it is evident that k_a cannot exceed 10^{-14} .

$\text{N}(\text{CH}_3)_3\text{Cl}.\text{CH}_2.\text{COOC}_2\text{H}_5$, *Betaine Ethyl Ester Chloride*.

This salt was prepared by adding an equivalent of methyl chloracetate to a solution of trimethylamine in absolute alcohol. After standing some time the alcohol was partially evaporated off, and on cooling, the substance separated out as white extremely hygroscopic crystals, which melted at 143° to 144° , with decomposition:—

0.2165 gramme gave ammonia equivalent to 0.0159	
gramme N	7.35 per cent.
Chlorine found	19.67 „
$\text{N}(\text{CH}_3)_3\text{Cl}.\text{CH}_2.\text{COOC}_2\text{H}_5$ requires N = 7.71, Cl ...	19.55 „
$\text{N}(\text{CH}_3)_3\text{Cl}.\text{CH}_2.\text{COOCH}_3$ „ N = 8.36, Cl ...	21.20 „

The substance by its composition and melting-point was thus proved to be the ethyl ester chloride, the formation of which was due to the choice of ethyl alcohol as solvent.*

Determination of Basic Constant—Catalysis Method.

I.

0.315 gramme substance in 15 c.c. water, 1 c.c. MeAc, $v = 8.64$, $A = 15.40$.

<i>t.</i>	Titre.	<i>x.</i>	$A - x.$	<i>c.</i>
0	0.12	0	15.40	—
11,117	3.65	3.53	11.87	0.0000102
12,564	4.02	3.90	11.50	101
14,072	4.50	4.38	11.02	103
15,583	5.00	4.88	10.52	106
16,868	5.33	5.21	10.19	106
Mean				0.0000103

* Compare Koeppen, 'Berichte,' vol. 38, p. 167, 1905.

1906.] *The Affinity Constants of Amphoteric Electrolytes.* 101

II.

0.2945 gramme substance in 15 c.c. water, 1 c.c. MeAc, $v = 9.24$, $A = 15.40$.

t .	Titre.	x .	$A-x$.	c .
0	0.13	0	15.40	—
9,790	3.35	3.22	12.18	0.0000104
11,243	3.80	3.67	11.73	105
12,751	4.30	4.17	11.23	107
14,262	4.76	4.63	10.77	109
15,547	5.17	5.04	10.36	110
Mean				0.0000107

N/15 Cl solution (5 per cent. HCl, 95 per cent. KCl), $c = 0.0000102$.

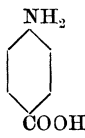
$$\text{From I—} \quad \frac{k_b}{K} = \frac{0.97 \times 8.64}{0.0290^2} = 9900.$$

$$\text{And from II—} \quad \frac{k_b}{K} = \frac{0.968 \times 9.24}{0.0323^2} = 8600.$$

Mean value for $k_b/K = 9000$.

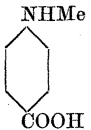
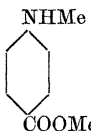
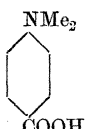
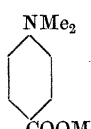
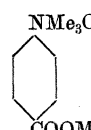
This value can only be regarded as approximate, owing to the length of time over which the action extended.

Summary of Results.

	k_a .	k_a/K .	k_b .	k_b/K .
*1. 	1.21×10^{-5}	1×10^9	2.54×10^{-12}	210
2. 	—	—	2.42×10^{-12}	200
3. 	—	—	2.88×10^{-12}	238

* The values pertaining to the substances marked with an asterisk are derived from Winkelblech's measurements (*loc. cit.*), and, except in the case of *p*-aminobenzoic acid, are not strictly comparable with my results.

102 *The Affinity Constants of Amphoteric Electrolytes.*

	k_a .	k_a/K .	k_b .	k_b/K .
4. 	0.92×10^{-5}	0.76×10^9	1.66×10^{-12}	137
5. 	—	—	2.08×10^{-12}	173
6. 	0.94×10^{-5}	0.778×10^9	3.25×10^{-12}	269
7. 	—	—	3.34×10^{-12}	276
8. 	$ca. 10^{-14}$	—	3.23×10^{-11}	2667
9. 	—	—	Very great	Very great
*10. $\text{CH}_2 < \begin{smallmatrix} \text{NH}_2 \\ \text{COOH} \end{smallmatrix}$...	3.4×10^{-10}	28,100	2.94×10^{-12}	243
11. $\text{CH}_2 < \begin{smallmatrix} \text{NH}_2 \\ \text{COOMe} \end{smallmatrix}$...	—	—	2.2×10^{-10}	18,000
*12. $\text{CH}_2 < \begin{smallmatrix} \text{NHMe} \\ \text{COOH} \end{smallmatrix}$...	1.3×10^{-10}	10,750	1.77×10^{-12}	146
13. $\text{CH}_2 < \begin{smallmatrix} \text{NMe}_2 \\ \text{COOH} \end{smallmatrix}$...	1.4×10^{-10}	12,000	1.06×10^{-12}	88
14. $\text{CH}_2 < \begin{smallmatrix} \text{NMe}_3 \\ \text{COO} \end{smallmatrix}$...	$ca. 10^{-14}$	—	8.7×10^{-13}	72
15. $\text{CH}_2 < \begin{smallmatrix} \text{NMe}_3\text{OH} \\ \text{COOEt} \end{smallmatrix}$	—	—	11×10^{-11}	9000 (?)

* The values pertaining to the substances marked with an asterisk are derived from Winkelblech's measurements (*loc. cit.*), and, except in the case of *p*-aminobenzoic acid, are not strictly comparable with my results.